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AUTHOR(S): P. J. Hay
C. M. Rohlfing

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Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

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Electronic Structure and Reactions of Transition Metal Complexes Using Effective Core Potentials

P. Jeffrey Hay and Celeste McMichael Rohlfing

Theoretical Division, MS-J569

Los Alamos National Laboratory

Los Alamos, New Mexico USA 87545

ABSTRACT. Effective core potentials are employed to study the geometries and binding energies of the species MCO and $M(CO)_4$ for M=Ni, Pd and Pt, and addition reactions of H_2 to $W(d^6)$ and $Pt(d^{10})$ centers. Møller-Plesset perturbation theory is assessed as a means of incorporating electron correlation effects in transition metal species.

1. INTRODUCTION

A theoretical understanding of the structures, chemistry, and photochemistry of transition metal complexes will require the reliable calculation of geometries and relative energies of the reactants, products, and transition states. In this report we summarize some of the recent advances employing effective core potentials (ECP's) for carrying out electronic structure calculations on transition metal species and we present representative examples in the above areas.

The ECP's employed in these calculations rigorously replace the core electrons by an effective one-electron potential that is required to produce a nodeless pseudo-orbital ϕ, which has the same orbital energy (ϵ_i) as the Hartree-Fock orbital (ϕ_i), and which has the identical shape as ϕ_i in the valence region of the atom. In addition, for the heavier elements (Z > 36), the relativistic mass velocity and Darwin terms are implicitly incorporated into the

relativistic effective core potentials (RECP), which are derived from all-electron relativistic Hartree-Fock calculations.

Recently, we have published a series of ECP's in analytic form for integral evaluation and the corresponding basis sets for the valence orbitals.[1-3] These include the transition metals Sc-Hg and the main group elements Na-Bi. A third series of ECPs was generated for the elements K-Hg including the outer "core" orbitals. In cases such as the K atom, where the "core" 3s and 3p orbitals can overlap significantly with electrons on other atoms, the core approximation breaks down and these electrons must be explicitly included along with the other valence electrons.

2. STRUCTURES AND ENERGIES OF METAL CARBONYLS

We have recently completed a systematic study of the transition metal monocarbonyls MCO and tetracarbonyls $M(CO)_4$ for M=Ni, Pd and Pt employing ECP's on the metal atoms. A 4-31G basis was used on C and O, and a [1s, 1p, 2d] contracted basis was used to describe the nd and (n+1)s,p orbitals of the metal. Geometry optimizations were carried out at the Hartree-Fock (HF) level, and also at the second-order Møller-Plesset perturbation theory (MP2) level to assess the effects of electron correlation. Other recent investigations on NiCO include ECP calculations by Rives and Fenske[5] and all-electron calculations by Ha and Nguyen[6] and by Blomberg et al.[7] All-electron studies of $Ni(CO)_4$ with geometry optimization include Faegri and Almlof[8] and Blomberg et al.[4] A more thorough review of the literature, including the Pd and Pt species, is given in Ref. 4.

Table 1 gives the geometries and dissociation energies of the $^1\Sigma^+$ state of the monocarbonyls. We shall examine the SCF results first. The r(M-C) bond lengths fall in the predicted order, Ni < Pd < Pt. The r(C-O) distances are

slightly longer than that in free CO, indicating that some backbonding to the CO π^* is occurring. The Pd and Pt compounds have similar r(C-O) separations, while in the Ni complex this distance is longer. This is in accord with stronger π back-donation in NiCO than in PdCO and PtCO as suggested by the metal atom ionization potentials. SCF dissociation energies relative to ^1S metal plus free CO yield the same relative stabilities as experiment, i.e., NiCO > PtCO $\geq$ PdCO. The MP2 results parallel exactly all of the trends found at the SCF level. Inclusion of correlation strengthens the M-C interaction through increased backbonding, thus shortening r(M-C) and lengthening r(C-O). The increased importance of π back-donation at the MP2 level is shown by the substantial lengthening of the monocarbonyl r(C-O) relative to MP2-optimized free CO. The magnitude of this r(C-O) stretch is much larger than the corresponding lengthening observed at the SCF level. The SCF-to-MP2 changes in the monocarbonyl r(C-O)'s are also larger than the corresponding change in free CO.

For the $^3\Delta$ states no bonding is apparent at the SCF level, while MP2 optimization yields weakly bound states for NiCO and PtCO with M-C bond lengths of 2.2 and 2.4 Å, respectively. Thus the ground state of linear MCO is predicted to be $^1\Sigma^+$.

Table II lists the bond lengths and dissociation energies calculated for the $^1A_1$ states of $Ni(CO)_4$, $Pd(CO)_4$, and $Pt(CO)_4$. First, the trend in the SCF r(M-C) bond length, Ni < Pd < Pt, is as expected, and follows that for the $^1\Sigma^+$ monocarbonyls, with the Pd-C and Pt-C bond lengths being similar. The relative stabilities as predicted by the SCF dissociation energies are $Ni(CO)_4$ > $Pt(CO)_4$ > $Pd(CO)_4$, in agreement with experiment.

MP2 geometry optimizations were performed for $Ni(CO)_4$ and $Pt(CO)_4$, and it was found that the r(C-O) bond length was nearly the same for both molecules. Hence only the Pd-C distance was optimized at the MP2 level for $Pd(CO)_4$.

Relative to the SCF results, the MP2 r(M-C) bond lengths are shorter due to increased backbonding, and the r(C-O) bond lengths are longer. MP2 increases the latter by 0.05 Å to a distance slightly longer than that in MP2-optimized free CO. The metal-carbonyl interaction is still weaker than that in $^1\Sigma^+$ MCO, since the average bond strengths in the tetracarbonyls are calculated to be 2.41, 1.25, and 1.46 eV for Ni, Pd, and Pt, respectively. This is not an unexpected result since there exists a competition among four equal ligands in the tetracarbonyls.

The agreement between experiment and the results in Table II is satisfactory. The relative stabilities of the three tetracarbonyls are predicted correctly. The MP2 bond lengths and strengths for $Ni(CO)_4$ agree fairly well with the experimental values, considering the basis set size and method of correlation. In conclusion, SCF and MP2 yield parallel trends. Correlation effects are very similar between the mono- and tetracarbonyls. The Pd species are found to be the least stable of the series Ni, Pd, and Pt.

TABLE I. Results for the $^1\Sigma^+$ state of MCO and the $^1\Sigma^+$ state of CO. Bond lengths in Å and dissociation energies in eV.

		R(M-C)	R(C-O)	D_e(to ^{1}S M)	D_e(to ^{3}D M)
NiCO	SCF	1.844	1.134	1.30	-3.44
	MP2	1.711	1.208	4.05	2.52
	expt.[a]	--	--	2.97	1.23
				±0.65	±0.65
PdCO	SCF	2.056	1.130	0.57	0.44
	MP2	1.882	1.185	1.62	2.48
PtCO	SCF	2.073	1.129	0.86	-0.18
	MP2	1.977	1.184	1.93	1.62
CO	SCF	--	1.128	--	--
	MP2	--	1.172	--	--
	expt.[b]	--	1.128	--	--

[a] Reference 9.

[b] K. P. Huber and G. Herzberg, Constants of Diatomic Molecules (Van Nostrand Reinhold Co., New York, 1979.)

TABLE II. Results for $^1A_1$ state of $M(CO)_4$. Bond lengths in A and dissociation energies in eV.

M		R(M-C)	R(C-O)	D_e(to ^1S M)
Ni	SCF	1.971	1.129	3.10
	MP2	1.873	1.181	9.64
	expt.[a)]	1.82-1.84	1.12-1.15	6.96-7.81
Pd	SCF	2.169	1.128	1.64
	MP2	2.032	(1.178)	4.98
Pt	SCF	2.202	1.128	2.22
	MP2	2.100	1.178	5.82

[a)] See Reference 4 for a summary of the experimental results.

3. ADDITION REACTIONS OF H_2 TO METAL CENTERS

The well-established oxidative addition reaction of H_2 to metal centers

$$ML_n + H_2 \rightarrow L_nMH_2$$

has often been postulated in catalytic cycles. The reaction has been observed for d^8 and d^{10} complexes. The model reaction for ML_n=$Pt(PH_3)_2$ has been studied by numerous investigators[10-12] using Hartree-Fock and correlated wavefunctions and employing relativistic ECP's on the Pt atom. Earlier calculations[10,11] showed the stable existence of the cis - L_2MH_2 species, the initial species formed in this reaction. Although the trans form appears to be the more stable, particularly with bulky PR_3 groups, the cis form has been detected recently in solution.

Table III summarizes the results of the various studies to date including the present results with the recent[1] ECP for Pt. The previous studies[10-12], which did not use "norm-conserving" ECP's, differ in the basis sets employed and (in the case of Ref. 10) in the geometry constraints assumed in the calculations.

Recently Kubas et al.[14] have prepared 5-coordinate compounds $M(PR_3)_2(CO)_3$, where M=Mo and W, that reversibly add hydrogen. Preliminary x-ray diffraction studies indicated that the H_2 bond remained intact, in contrast to the usual situation discussed above for d^8 and d^{10} complexes. Ab initio studies[15] were carried out on various geometries of the model compound $W(PH_3)_2(CO)_3$ including 6-coordinate side-on bonded and end-on bonded H_2 forms and the 7-coordinate dihydride form. The side-on bonded forms were found to be stable relative to the $WL_5 + H_2$ fragments by 17 kcal/mole. The lowest energy form (1) had the H-H axis parallel to the P-W-P axis but with very little barrier (0.3 kcal/mole) to

rotation about the W-H_2 axis (Table IV). The W-H distance was calculated to be 2.15 Å at the Hartree-Fock level and the H-H separation was found to be 0.79 Å, only 0.05 Å longer than in H_2 itself. The published structure[14] showed inequivalent W-H bonds of 1.76 and 2.12 Å and an H_2 distance of 0.75 ± 0.16 Å from low temperature x-ray diffraction. Room temperature neutron diffraction studies suggested R(W-H) = 1.75 Å and R(H-H) = 0.86 Å, although there were problems arising from disorder in the crystal. More recent unpublished low temperature neutron diffraction studies show equivalent W-H bonds 1.89 ± 0.01 Å in length, an H_2 separation of 0.82 ± 0.01 Å, and the H_2 lying parallel to the P-W-P axis in accord with the theoretical results.

Calculations on the as-yet unobserved 7-coordinate dihydride,[5] corresponding to the oxidative addition product, find it 17 kcal/mole higher than the side-on bonded form--or nearly equal to the energy of the separate fragments. When PH_3 groups are substituted for the π-accepting CO groups, we find the oxidative addition is 2 kcal/mole exothermic, compared with 17 kcal/mole emdothermic when three CO ligands are present. These results suggest that ligand substitution could be used to favor either the dihydrogen or dihydride forms. Experimentally, 7-coordinate $Mo(PR_3)_5(H)_2$ complexes have been observed to support this hypothesis.

TABLE III. Reaction energies (E_{react}), activation energies (E_{act}), and Pt-H distances for the transition state in the $Pt(PH_3)_2 + H_2$ reaction.

	E_{react}	E_{act}	Transition State R(Pt-H)
	(kcal/mole)	(kcal/mole)	(Å)
	Hartree-Fock Wavefunctions		
Noell, Hay[10]	-16	17	1.81
Kitaura et al.[11]	-37	5.2	2.07
Low, Goddard[12]	-6.7	4.0	2.20
Hay	-4.2	8.4	1.70
	Correlated Wavefunctions		
Noell, Hay[10]	-5.0	16.6	[1.76]
Kitaura et al.[11]	-27	7.1	[2.07]
Low, Goddard[12]	-15.9	2.3	2.42
Hay--MP2	7.5	0.8	[1.70]
Hay--MP3	-8.6	4.0	[1.70]

TABLE IV. Relative energies of various forms of $W(L_1)_3\ (L_2)_2\ (H_2)$ complexes.

	Relative energy, (kcal/mole)	R(W-H), (A)
L_1 = CO, L_2 = PH_3		
Side-on complex	0.0	2.15
Side-on complex	0.3	2.18
End-on complex	11	2.44
Fragments	17	∞
7-Coordinate complex	17	1.89
L_1 = L_2 = PH_3		
Side-on complex	0	1.84
7-Coordinate complex	-2	1.84

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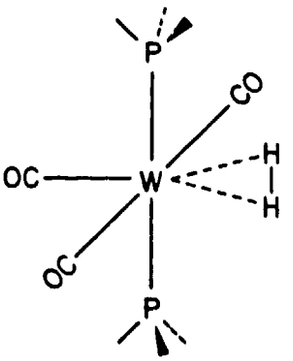
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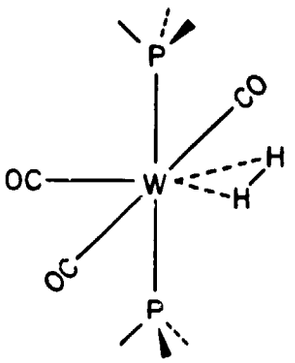
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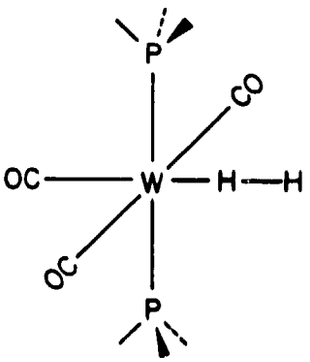
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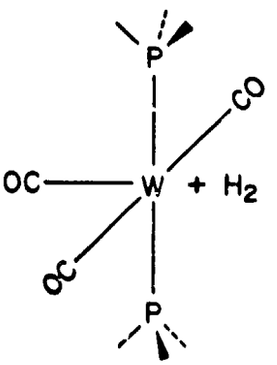
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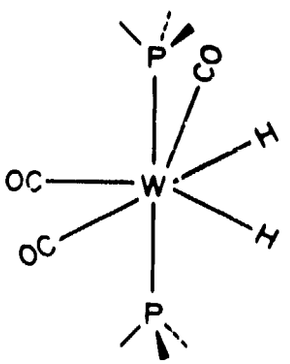
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